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13. ABSTRACT (Maximum 200 words)

This work developed chemical self-assembly methods for the fabrication of high dielectric oxide thin films and nanometer-scale electronic devices. The experimental emphasis was on preparation and testing of thin film dielectrics for memories, fabrication of single electron transistors, nucleation/growth of colloidal crystals, template synthesis of metal nanowires, and synthesis/combinatorial selection of alloy nanocrystals for chemical sensor applications. The thin film assemblies were deposited chemically from building blocks with characteristic dimensions of nanometers to microns: lamellar inorganic dielectrics, sol-gel metal oxide monolayers, polymer chains, colloidal metal and semiconductor particles, and nanowires. Thin films were grown by colloid adsorption, and by sol-gel processing of molecular precursors. Understanding and controlling self-assembly in these systems required theoretical development and computer simulations. Much of the theoretical effort was devoted to issues of simulation and visualization of particle self-assembly in one and two dimensions. Dynamical lattice gas modelswere developed, in order to model the assembly of mesoscopic particles. Two important successes of this project were (1) development of methods for making patterned, high dielectric thin film oxides by combining microcontact printing with inorganic self assembly, and (2) development of a combinatorial technique for identifying highly active alloy nanoparticle catalysts for amperometric sensors.

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Final Progress Report, DAAH04-96-1-0180

***Three Dimensional Self-Assembled Electronic Nanostructures and Materials from Molecular Precursors***

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## Problems Studied

This project developed self-assembly techniques for electronic devices and materials, focusing particularly on nanoscale inorganic particles as building blocks of thin films. One of the motivations for this work was to find novel ways to make thin films of high dielectric materials for use in DRAM capacitors and related devices Lamellar colloids were made by chemical exfoliation of layered titanates, tantalates, and niobates, and were grown layer by layer on surfaces by using wet chemical techniques. The condensation of these lamellar colloids into continuous films was studied, as was the preparation of continuous films from sol-gel precursors. The dielectric properties of the lamellar solids and films was studied, revealing some new low loss, high dielectric materials. Layered Coulomb blockade devices were prepared by similar methods and characterized. Nanoscale wires were also made by template electrochemical replication and initial studies of their self-assembly on surfaces were conducted. Finally, a method was developed for combinatorial discovery and optimization of new electrode materials for amperometric chemical and biochemical sensors.

## Summary of Most Important Results

*Self-assembled Coulomb blockade devices.* Metal-insulator-nanoparticle-insulator-metal (MINIM) devices were prepared by self-assembly, from colloids of lamellar insulators, gold particles, and polymers. With sufficiently thin insulator layers (30-90 Å) a Coulomb gap is observed in the i-V characteristic. This behavior arises from single electron charging of the gold nanoparticles. The most remarkable feature of these devices is that there is an insignificant density of short circuits in a 1 $cm^2$ array containing approximately $10^{11}$ parallel

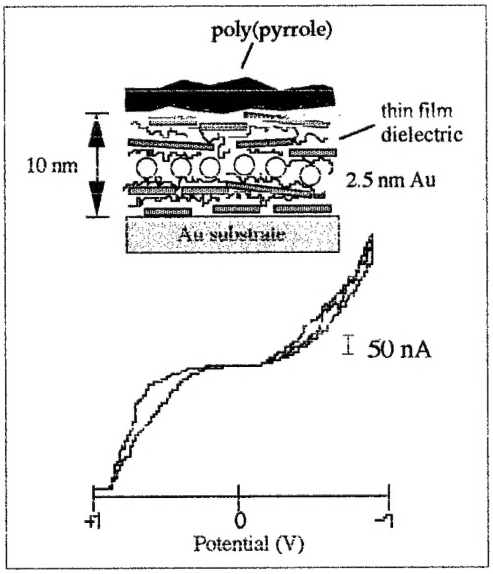


Figure 1. Structure of a Coulomb blockade device made by layer-by-layer adsorption of insulator colloids and metal nanoparticle layers. The colloidal sheets are made by exfoliation of lamellar solids ($\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ or $HTiNbO_5$). The top contact is also grown chemically, from by oxidation of pyrrole vapor.

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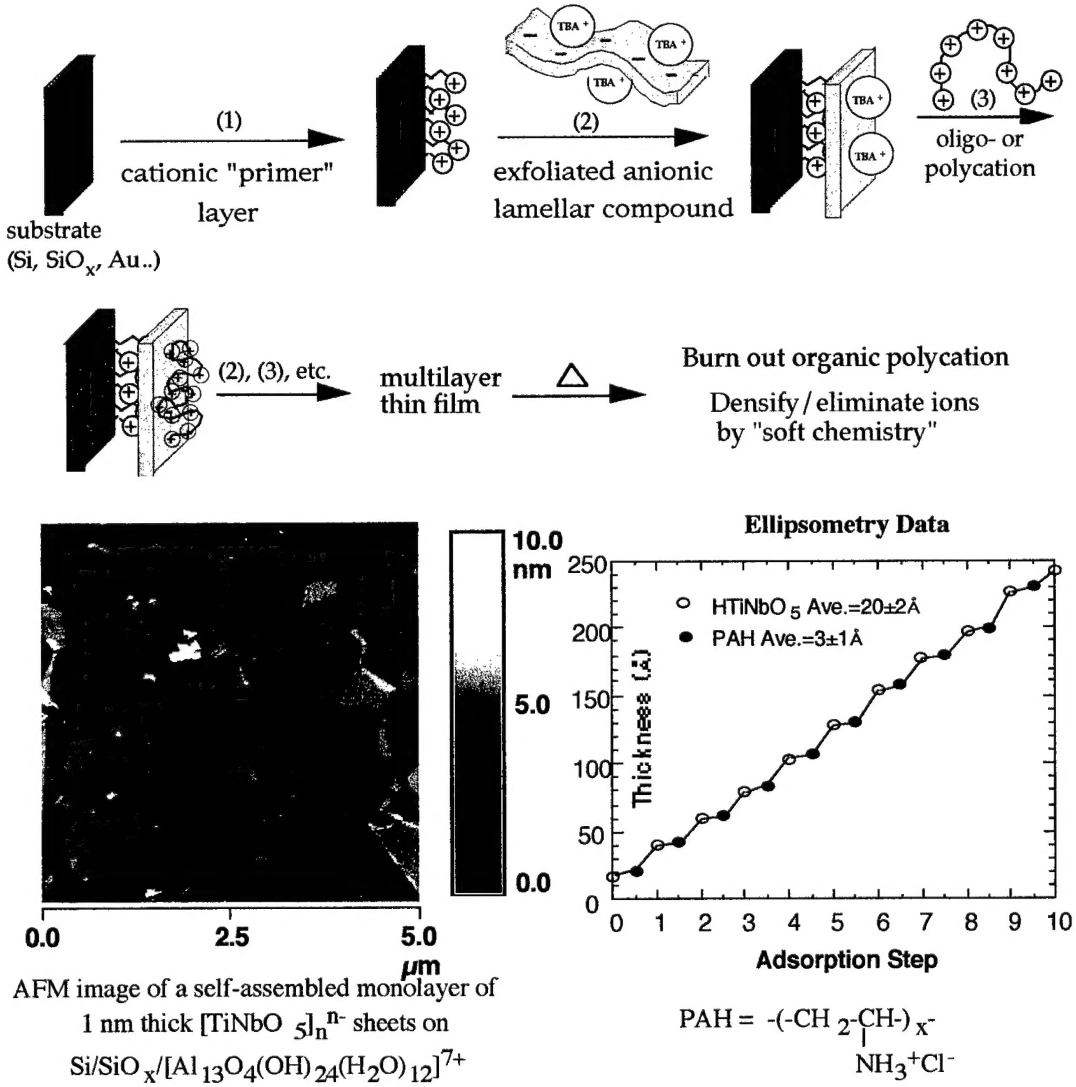
tunnel junctions, despite the fact that they are made entirely by "benchtop" chemical techniques. Angle-resolved XPS experiments confirm the lamellar structure of these devices. Figure 1 shows a cartoon of the structure as determined by XPS, and the i-V characteristics of a room temperature device made from 2.5 nm Au nanoparticles.

Theory predicts, and experimental data confirm, the dependence of the size of the Coulomb gap on temperature, insulator thickness, and nanoparticle diameter. The temperature dependence of the i-V behavior is currently being studied as a function of insulator and nanoparticle dimensions. Theoretical calculations by Korotkov and Likharev suggest that the i-V characteristics of Coulomb blockade devices should be improved by using "staircase" barriers, which consist of insulators of different barrier heights. We are currently




AFM image of a self-assembled monolayer of 1 nm thick $[TiNbO_5]_n^{n-}$ sheets on $Si/SiO_x/[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$

PAH = -(-CH$_2$-CH-)$_x$-
$NH_3^+Cl^-$

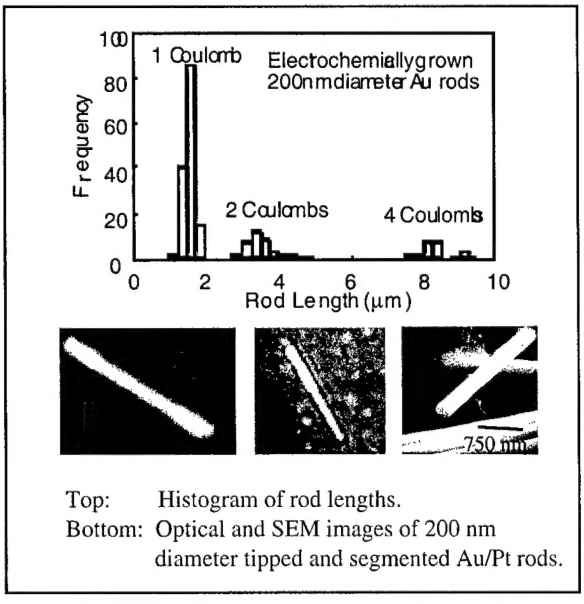
Figure 2. Top: Reaction scheme for layer-by-layer growth of high dielectric oxide films from lamellar colloids. Bottom: AFM image of the tiling of a surface by 1 nm thick $HTiNbO_5$ sheets, and ellipsometric thickness plot for layer-by-layer film growth.

investigating this possibility using insulator and metal nanoparticle layers grown sequentially as segments of metal nanorods in porous membranes (see below).

*Layer-by-layer assembly of high dielectric oxide thin films.* Representative high dielectric lamellar solids (in particular layer perovskite titanates, niobates, and tantalates) were grown as monolayer (1-2 nm) and multilayer thin films by ionic self-assembly. The dielectric properties of the lamellar solids and their condensation products were studied by complex impedance techniques. In bulk form, several of these materials have low-frequency dielectric constants in the 100-200 range; most exhibit high loss and decreasing dielectric constant at MHz and higher frequencies. However, a few, particularly acid-exchanged niobate layer perovskites, have low loss at all frequencies. Techniques were developed to eliminate ions from the thin films by burnout of organic components and dehydration/condensation reactions. This reaction scheme is illustrated in Figure 2.

*Surface sol-gel synthesis of titanate and tantalate thin films.* A layer-by-layer sol-gel process was developed for growing high dielectric Ti-Ta oxide ultrathin films. Patterned arrays of 1-10 nm thick oxides have been made by combining this sol-gel technique with microcontact printing (μ-CP). AFM and SEM images show that the films are smooth and free of cracks or pinholes. However, as grown they are less dense than the corresponding bulk oxides and do not adhere well to Si. Annealing at 400°C densifies the oxides and makes adherent thin films.

*Preparation of rod colloids by replication of porous membranes.* Rod colloids were made by electrochemical replication of porous alumina membranes. Monodisperse samples of "striped" and "tipped" 200 nm diameter Au/Pt rods are being studies as building blocks of three-dimensional woodpile architectures. The length of the individual segments (Au or Pt) can be controlled to ± 10% by controllingthe electrodeposition time. Orthogonal self-assembly experiments have been done to show that the tips of Au-Pt-Au rods can be selectively derivatized with thiol-terminated fluorescent dyes, while the Pt barrels of the rods are rendered non-adhesive using a butylisonitrile monolayer. Electronic transport measurements on individual Au rods show that their conductivity is about one order of magnitude lower than bulk annealed Au. Current experiments, supported under the DARPA Moletronics program, focus on making Au/molecule/metal two-terminal devices, and on self-assembling rod arrays on lithographically patterned substrates by DNA hybridization.




Top: Histogram of rod lengths.
Bottom: Optical and SEM images of 200 nm diameter tipped and segmented Au/Pt rods.

Figure 4. Results of templated electrochemical growth of metal nanorods from porous alumina membranes. Top: Rod length is controlled coulometrically. Bottom: cylindrical rods with pre-determined stripe patterns are produced by sequentially plating different metals.

*Dynamic lattice gas simulations.* Extensive simulations have been performed of one-dimensional lattice models for dynamical geometries relevant to nano- and micro-scale chemical self-assembly. These simulations have demonstrated the evolution of structure. Mean-field analysis of the models has begun and is being compared with the numerical results. An asynchronous two dimensional model for particles interacting with a triangulated surface has been constructed, but not yet simulated.

*Combinatorial Discovery and Optimization of Sensor Materials.* Although not part of our original proposal, ARO's interest in chemical and biochemical sensors, and progress in our laboratory on combinatorial catalysis, motivated us to attempt to adapt combinatorial techniques to the discovery of better sensor materials. As a proof of concept example we prepared and screened 715-member pentanary alloy arrays for activity as glucose oxidation catalysts. Screening was carried out by converting the current at each electrode spot to a fluorescence signal, taking advantage of the fact that catalytic glucose oxidation lowers the local pH. Figure 5 shows an activity map of one of the quaternary regions scanned. The most active compositions contained both Pt and Pb, which means that these two elements play key roles in glucose oxidation. Bulk quantities of catalysts with compositions corresponding to those identified in the screening experiments were prepared and characterized. The best alloy electrocatalysts catalyzed glucose oxidation at substantially more negative potentials than pure platinum in enzyme-free voltammetric measurements. They were also insensitive to potential interferents (ascorbic and uric acids, and 4-acetamidophenol), which are oxidized at slightly more positive potentials. Rotating disk electrode (RDE) experiments were carried out to study the catalytic mechanism. The improvement in catalytic performance was attributed to the inhibition of adsorption of oxidation products, such as gluconolactone, which poison Pt electrodes.

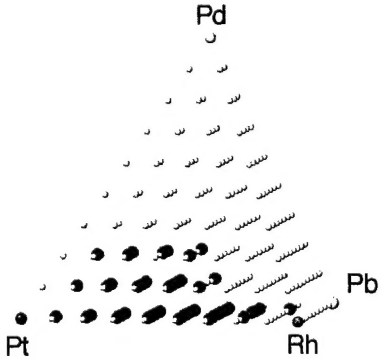



Figure 5. Activity map in the Pd-Pt-Rh-Pb composition space for electrocatalytic glucose oxidation. The most active catalysts are found near the Pt-Rh-Pb ternary face of the map.

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**Personnel Report**
August 1996-May 2000

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**Inventions**

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